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# ANALYSIS OF COLLOCATED SAMPLING RESULTS FOR VOLATILE ORGANIC COMPOUNDS

(includes Hamilton data)

JANUARY 1993

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Report Prepared For:

Air Resources Branch
Ontario Ministry of the Environment

JANUARY 1993

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# ANALYSIS OF COLLOCATED SAMPLING RESULTS FOR VOLATILE ORGANIC COMPOUNDS

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JANUARY 1993

## ACKNOWLEDGEMENT

Sample collection was carried out by personnel in West Central Region under the supervision of Neil Buonocore. Sample analyses were handled by the Laboratory Services Branch, Trace Organics Section, Air Unit, under the supervision of B. Foster.

## INTRODUCTION

In the spring of 1989 a three-site trial network of Volatile Organic Compounds (VOC) samplers was initiated. This network has grown substantially and now the Volatile Organic Compounds Monitoring Network consists of 14 sites across the province collecting samples on a 1 in 12 day schedule.

As part of the quality assurance efforts for the network, a roving duplicate sampler has been used to determine the reproducibility of the sampling and analytical methods. This report presents results for the calendar year 1991 when the duplicate sampler was installed in downtown Hamilton.

Specific details of the program and ambient air data listings are available elsewhere[1,2,3,4,5].

## DATA SCREENING

Data screening procedures are detailed in the ambient air data listing reports. However, the data used in this report have been subject to further screening. First; all samples for which the volume is less than 34.2 L or greater than 37.8 L have been removed. These limits correspond to a variation in flow rate of ± 5%, a realistic target if the flow controller is working properly. More likely, samples are rejected because of sampler failure (leading to a sample volume of only a few litres) or a timer problem (e.g. not shutting off the sampler after 24 hours).

Second; all results reported as <W have been replaced with ½ the W value. This practice has been shown to be not significantly different from various other "backfill" techniques provided less than 80% of the sample is reported as non-detects[6]. If more than 80% of the results for a specific compound are reported as <W then that compound is not included in the analysis.

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1 Ontario Ministry of the Environment Volatile Organic Compounds Monitoring Network Standard Operating Procedures and Technical Manual. Air Resources Branch Report # ARB-224-89, January 1990.

2 Volatile Organic Compounds Monitoring Network Quality Assurance Plan. Air Resources Branch Report # ARB-021-90.

3 Volatile Organic Compounds Monitoring Network Ambient Air Concentration Data Listing 1989. Air Resources Branch Report # ARB-105-92.

4 Volatile Organic Compounds Monitoring Network Ambient Air Concentration Data Listing 1990. Air Resources Branch Report # ARB-106-92.

5 Volatile Organic Compounds Monitoring Network Ambient Air Concentration Data Listing 1991. Air Resources Branch Report # ARB-113-92.

6 Steer, P. and G. Diamond. A proposal for handling non-detects in air monitoring data. Memorandum to the Windsor Air Toxics Study Technical Committee dated November 27, 1991.

RESULTS

The following compounds were never detected by either sampler: 1,1,2-trichloroethane (vinyl trichloride), chlorobenzene (phenyl chloride), 1,3-dichlorobenzene (m-dichlorobenzene), 1,2-dibromoethane (ethylene dibromide), and vinyl chloride (chloroethylene). An additional nine compounds were not detected more than 80% of the time. Table I shows the compound with the appropriate "W" value ($\mu g/m^3$), the number of samples, the number of non-detects (nd), and the maximum result ($\mu g/m^3$) from both sampler A and sampler B. [See Appendix A for a table of compound names and synonyms. Excluded are those compounds listed above.]

TABLE I. Compounds not detected more than 80% of the time.

| | | Sampler A | | Sampler B | |
|---|---|---|---|---|---|
| Compound | <W | n (nd) | max | n (nd) | max |
| 1,1-Dichloroethane | 0.1 | 17 (17) | nd | 17 (15) | 2.2 |
| 1,2-Dichloroethane | 0.1 | 17 (17) | nd | 15 (14) | 0.2 |
| Carbon tetrachloride | 0.8 | 17 (14) | 12.2 | 15 (12) | 3.2 |
| Trichloroethylene | 0.1 | 17 (14) | 0.4 | 16 (14) | 0.5 |
| 1,1,2,2-Tetrachloroethane | 0.2 | 17 (14) | 1.2 | 16 (13) | nd |
| 1,2-Dichlorobenzene | 0.1 | 16 (15) | 0.3 | 16 (15) | 0.7 |
| Acrylonitrile | 0.3 | 16 (15) | 0.4 | 17 (17) | nd |
| 1,2-Dichloropropane | 0.1 | 17 (15) | 0.7 | 16 (14) | 0.7 |
| cis-1,3-Dichloropropene | 0.1 | 17 (14) | 1.0 | 15 (13) | 1.0 |

Figure 1 shows scatter plots of results from sampler A vs results from sampler B for compounds detected more than 20% of the time. The plots are arranged in order from lower to higher boiling point and non-chlorinated to chlorinated VOC (the 1:1 line is also shown). Generally, there is least scatter about the 1:1 line for higher concentrations of non-chlorinated VOC. More scatter about the 1:1 line is apparent for concentrations closer to the detection limit and for chlorinated VOC (the exception is tetrachloroethylene). Identification and quantitation of chlorinated VOC is poorer with a flame ionization detector (FID) than with a mass selective detector (MSD). The FID was used for this study. Note also that most of the compounds that are routinely not detected by either sampler are chlorinated (Table I).

Three methods were used to compare results from the two identical samplers. The first method provides a measure of agreement (G) and is based upon the following conditions:

A) The result of the comparison should be a number between 0 and 100% where 100% represents complete agreement and 0% represents no agreement.

B) To accomplish (A) the result should be normalized in some manner; and

C) Since the samplers are indistinguishable and, in all likelihood, the samples may be confused from time to time, the comparison result should not depend on which sampler is arbitrarily defined as "independent" (Diamond, pers. comm.):

$$G = \left[ 1 - \frac{|A-B|}{A+B} \right] * 100$$

where A is the concentration of the analyte from the first sampler and B is the concentration of the analyte from the second sampler. Because this method provides a measure of *agreement*, numbers closer to 100 indicate better sampler performance.

The median absolute difference also gives an indication of the overall precision of collocated samplers:

$$\frac{\textit{Median}\ |A-B|}{\textit{Median}\ \overline{A+B}} * 100$$

where A and B are as previously defined. Note that this method yields *difference* (or disagreement) and thus numbers closer to zero indicate better sampler performance.

The third method of comparison used was the Wilcoxon signed rank test. This test is similar to the sign test, however, the signed rank test takes into account the magnitude of the difference between results rather than just the sign of the difference. At a 95% confidence level ($\alpha = 0.05$) the computed test statistic Z must be $\leq 1.96$ to accept the null hypothesis that there is no difference in the distributions of the two samples. The $\alpha$ value is the chance (5%) of incorrectly rejecting the null hypothesis (concluding that the samples are different when in fact they are not; a Type I error).

Results from all three tests are presented in Table II on the following page. For the median percent agreement and the median absolute difference cells are shaded if the compound falls outside an "acceptability" cut-off of ± 25% (i.e. 75% agreement or 25% disagreement). If the Wilcoxon test statistic is larger than 1.96 the cell is shaded. This indicates that the null hypothesis of similar sample distributions must be rejected; i.e. the samples come from different populations. Note that as the Wilcoxon test statistic approaches 0 the probability of equalling or exceeding the test statistic approaches 1. Note also that this test ignores tied pairs so the result for, say, naphthalene (12 tied pairs out of 15 total pairs) will be less meaningful than that for, say, benzene (2 tied pairs out of 16 total pairs).

Compounds for which the median percent agreement is 100.0 or the median absolute difference is 0.0 are those compounds for which the results are predominantly non-detects but not at the 80% level. Remember that compounds not detected more than 80% of the time are listed in Table I. Chloromethane and 1,3-butadiene tended to be not detected or detected at very low levels on one sampler but not the other and this causes poor comparability in the median absolute difference test and a low percent agreement in the median percent agreement test. It is for a similar reason that trichloromethane fails the Wilcoxon test. Bear in mind that the median percent agreement or disagreement is presented here; a somewhat less contradictory outcome for chloromethane, 1,3-butadiene, and trichloromethane might occur if the average were used rather than the median.

TABLE II. Compound specific results from three comparison tests. Median percent agreement, median absolute difference, and the Wilcoxon signed rank test.

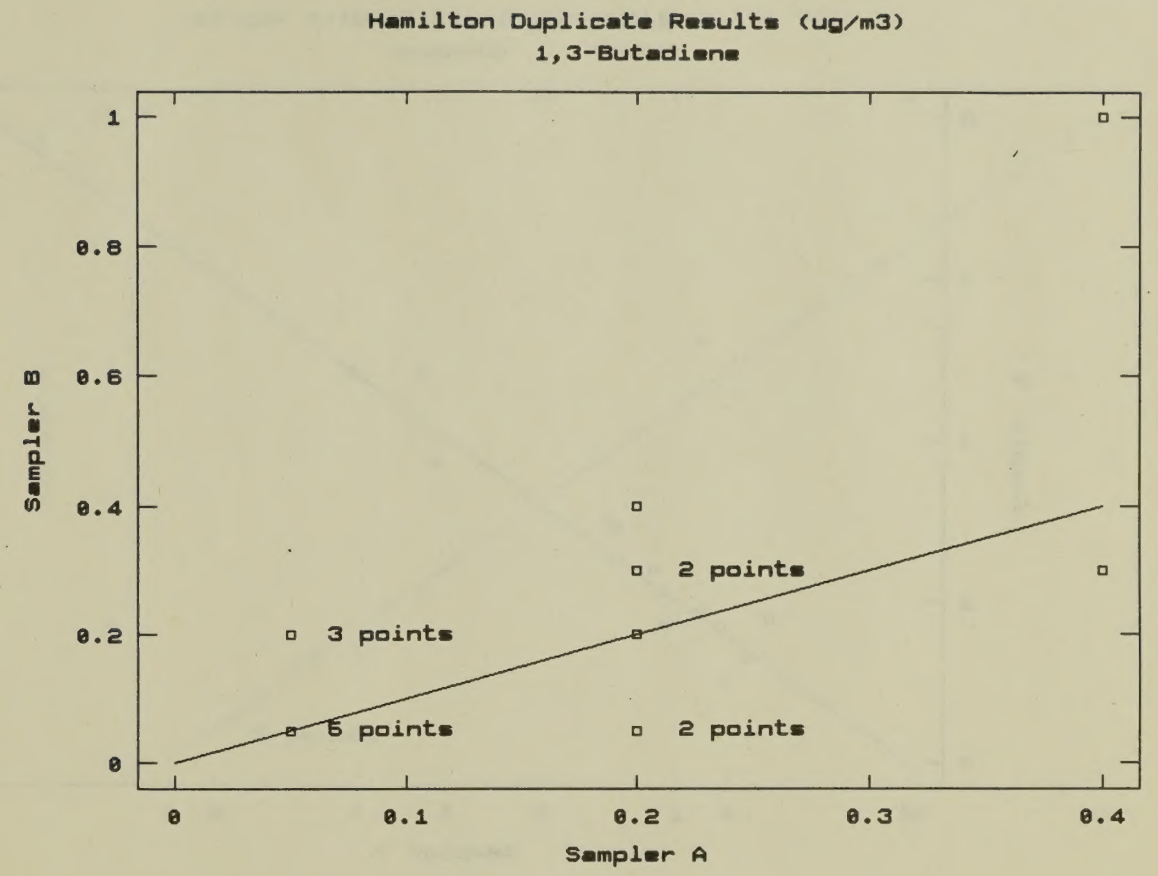
| Compound | Median % Agreement | Median Absolute Difference (%) | Wilcoxon Test Statistic |
|---|---|---|---|
| Naphthalene | 100.0 | 0.0 | 0.27 |
| Dichloromethane | 100.0 | 0.0 | 1.44 |
| 1,1,1-Trichloroethane | 90.9 | 20.7 | 1.19 |
| Benzene | 94.9 | 9.1 | 1.25 |
| Toluene | 95.3 | 10.6 | 0.14 |
| Tetrachloroethylene | 96.1 | 7.1 | 1.16 |
| Ethylbenzene | 94.7 | 9.3 | 1.29 |
| o-Xylene | 92.9 | 12.2 | 0.71 |
| 1,2,4-Trimethylbenzene | 92.0 | 15.1 | 0.56 |
| 1,3-Butadiene | 80.0 | 80.0 | 1.48 |
| Cyclohexane | 85.7 | 28.6 | 1.07 |
| Hexane | 97.5 | 4.2 | 1.24 |
| 1,3,5-Trimethylbenzene | 90.9 | 18.2 | 1.24 |
| m+p-Xylene | 96.5 | 5.9 | 0.77 |
| Styrene | 100.0 | 0.0 | 1.78 |
| Trichloromethane | 100.0 | 0.0 | 2.10 |
| Isoprene | 100.0 | 0.0 | 1.26 |
| Bromodichloromethane | 100.0 | 0.0 | 0.00 |
| Chloromethane | 75.0 | 64.3 | 2.38 |
| 1,1-Dichloroethene | 94.7 | 26.7 | 1.30 |
| 1,4-Dichlorobenzene | 85.7 | 28.6 | 1.12 |

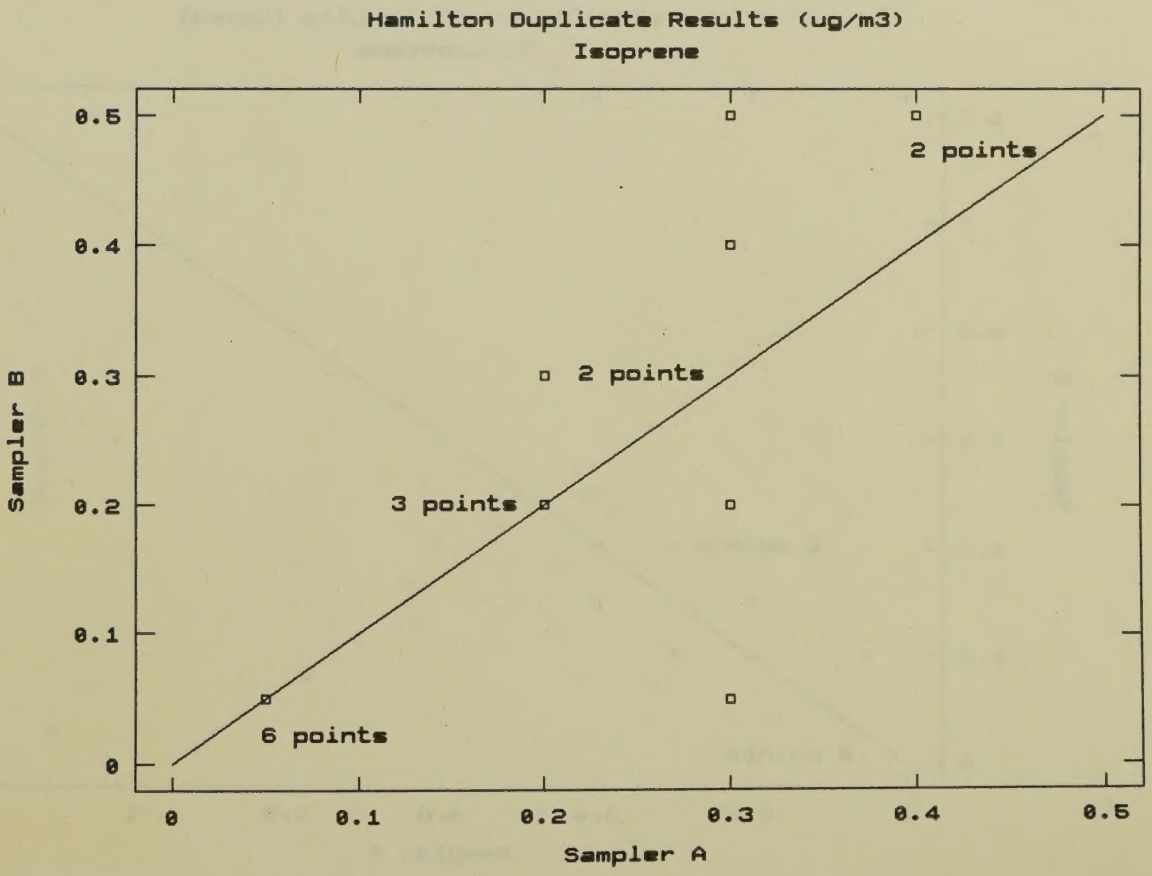
## CONCLUSIONS

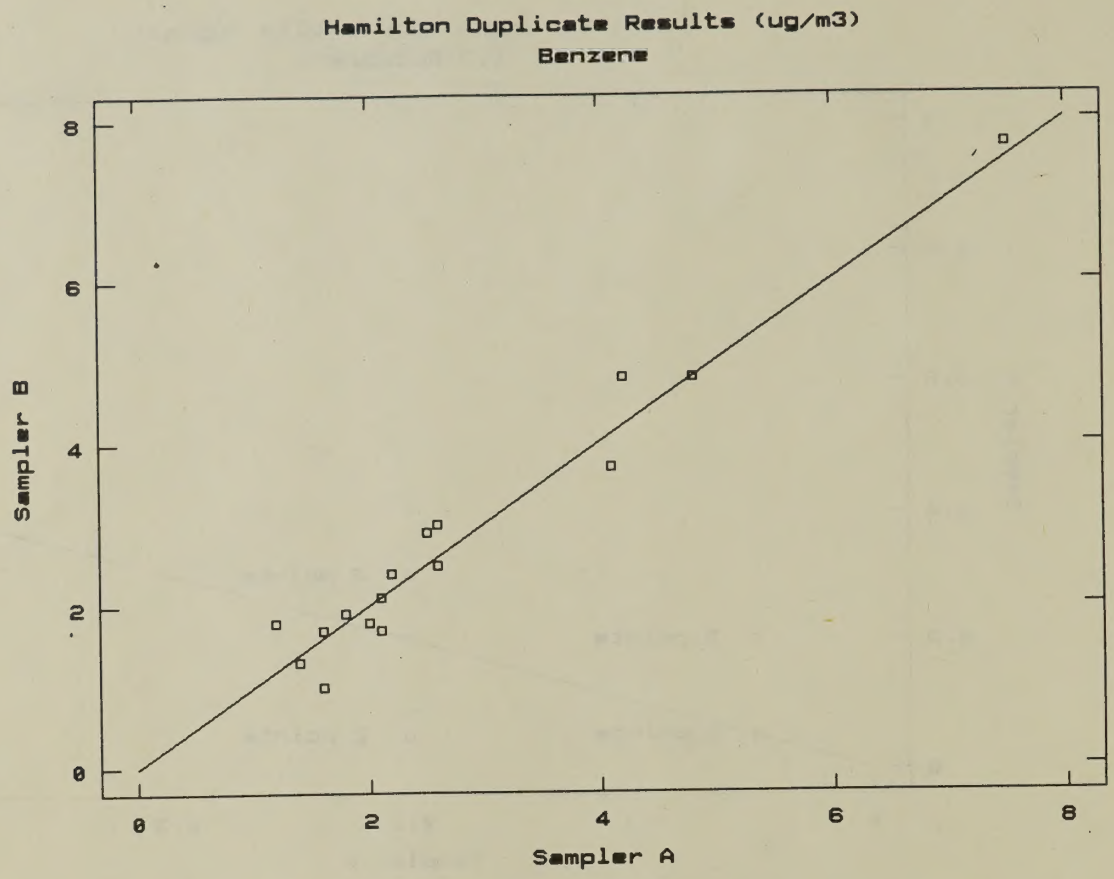
The methods for comparison used in this analysis give a measure of the overall precision of the VOC sampling method; i.e. the analytical stage is not separated from the sampling stage. The results presented above suggest that the precision of the VOC sampling/analytical method is very good. In future, the analytical finish will be by MSD and better identification and lower detection limits are expected. Although the precision of the method will drop for some chlorinated compounds and those compounds that are at or only slightly above current detection levels, the numbers should be more meaningful since the number of non-detects reported should

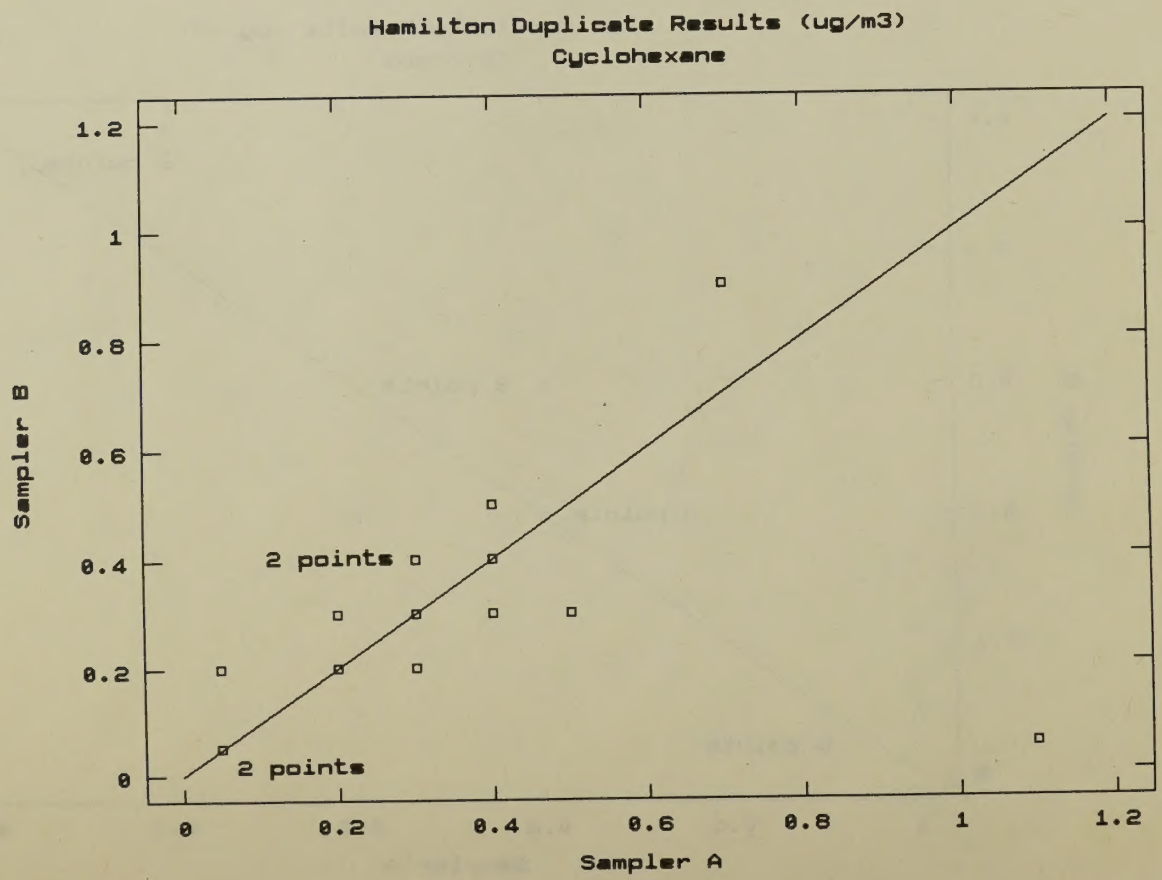
be fewer. The most obvious effect will be on the following compounds for which the median percent agreement or median absolute difference is already 100.0 or 0.0: naphthalene, dichloromethane, styrene, trichloromethane, isoprene, and bromodichloromethane.

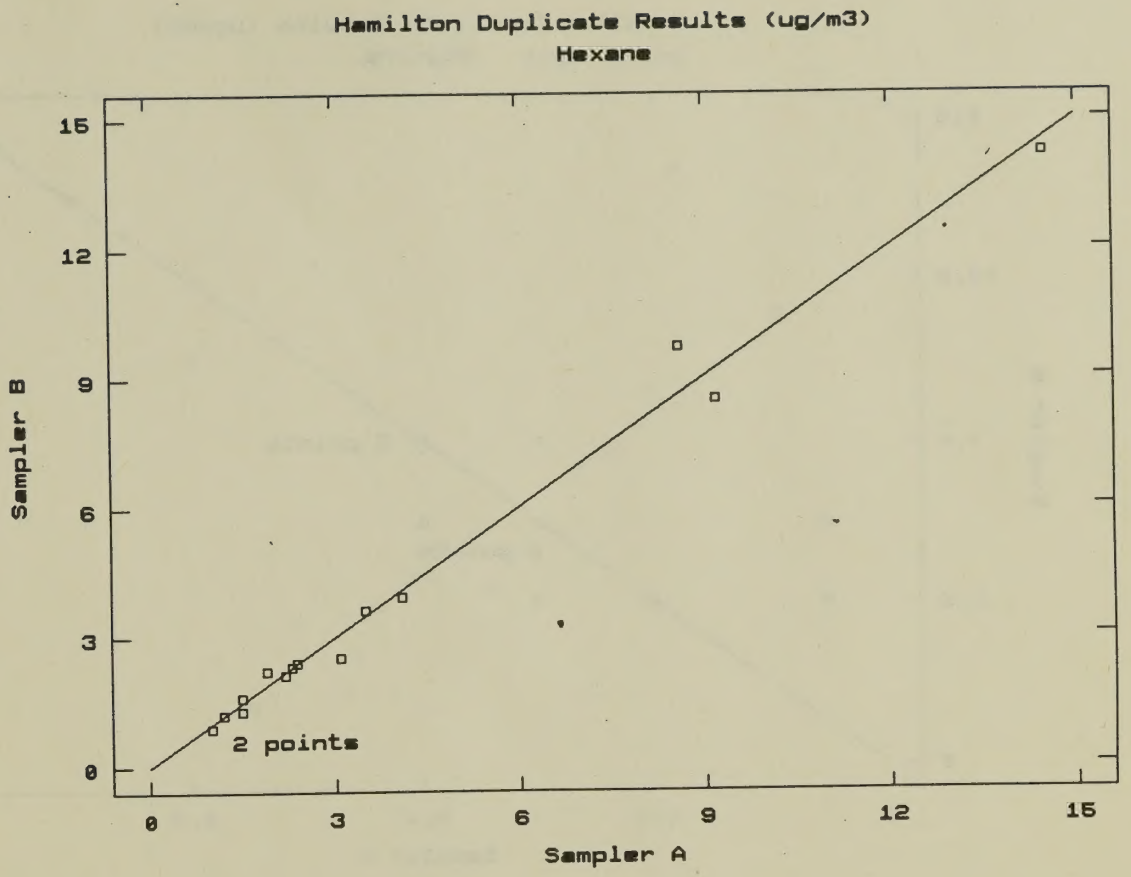
FIGURE 1. Scatter plot of concentration results from Sampler A vs Sampler B.

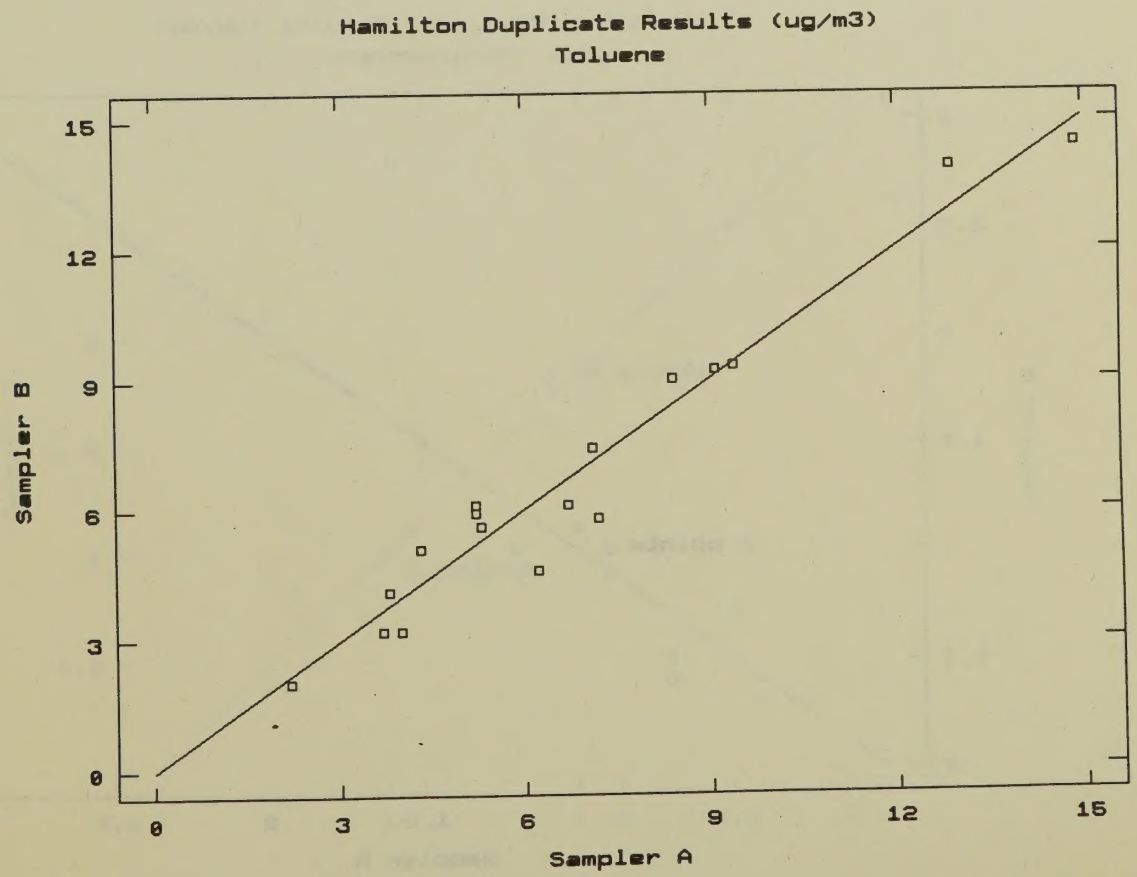

Hamilton Duplicate Results (ug/m3)
1,3-Butadiene
Sampler B
Sampler A
1
0.8
0.6
0.4
0.2
0
0
0.1
0.2
0.3
0.4
2 points
3 points
6 points
2 points

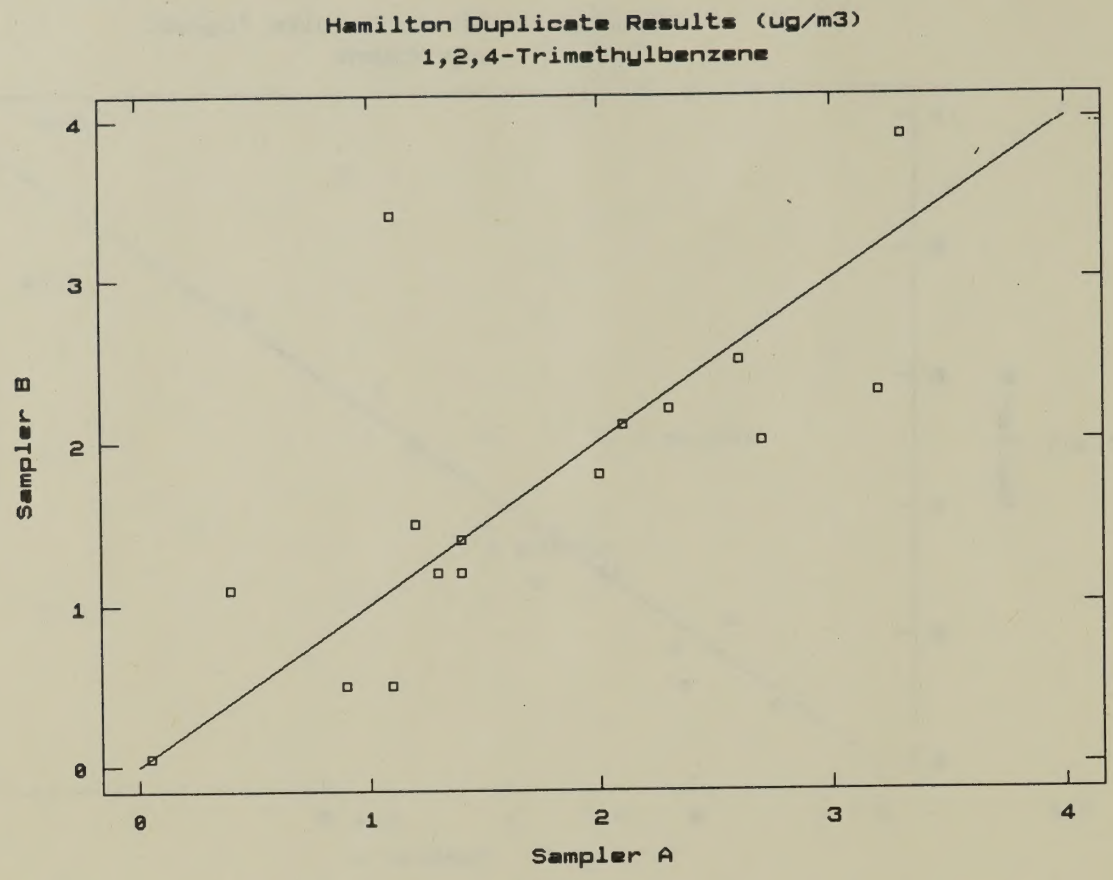

Hamilton Duplicate Results (ug/m3)
Isoprene
Sampler B
Sampler A
0.5
0.4
0.3
0.2
0.1
0
0
0.1
0.2
0.3
0.4
0.5
2 points
2 points
3 points
6 points

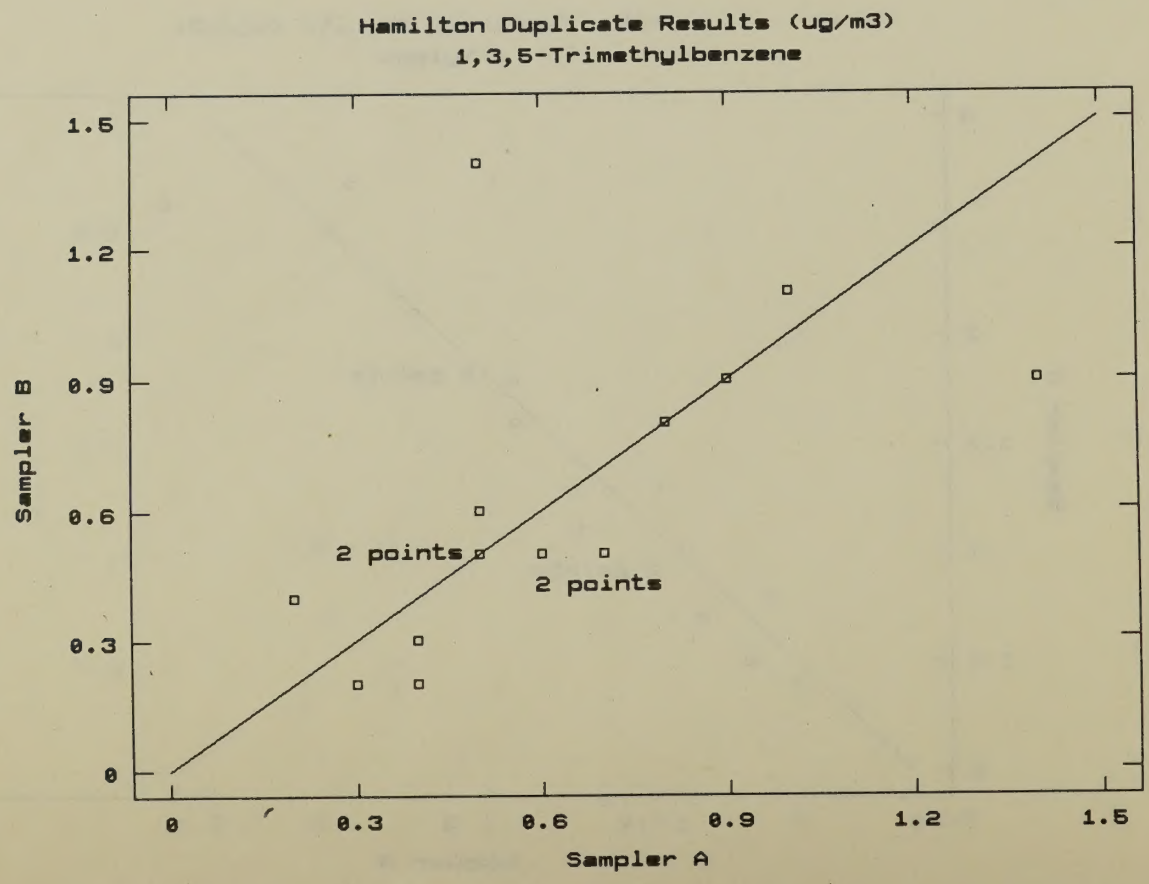

Hamilton Duplicate Results (ug/m3)
Benzene
Sampler B
Sampler A
0
2
4
6
8

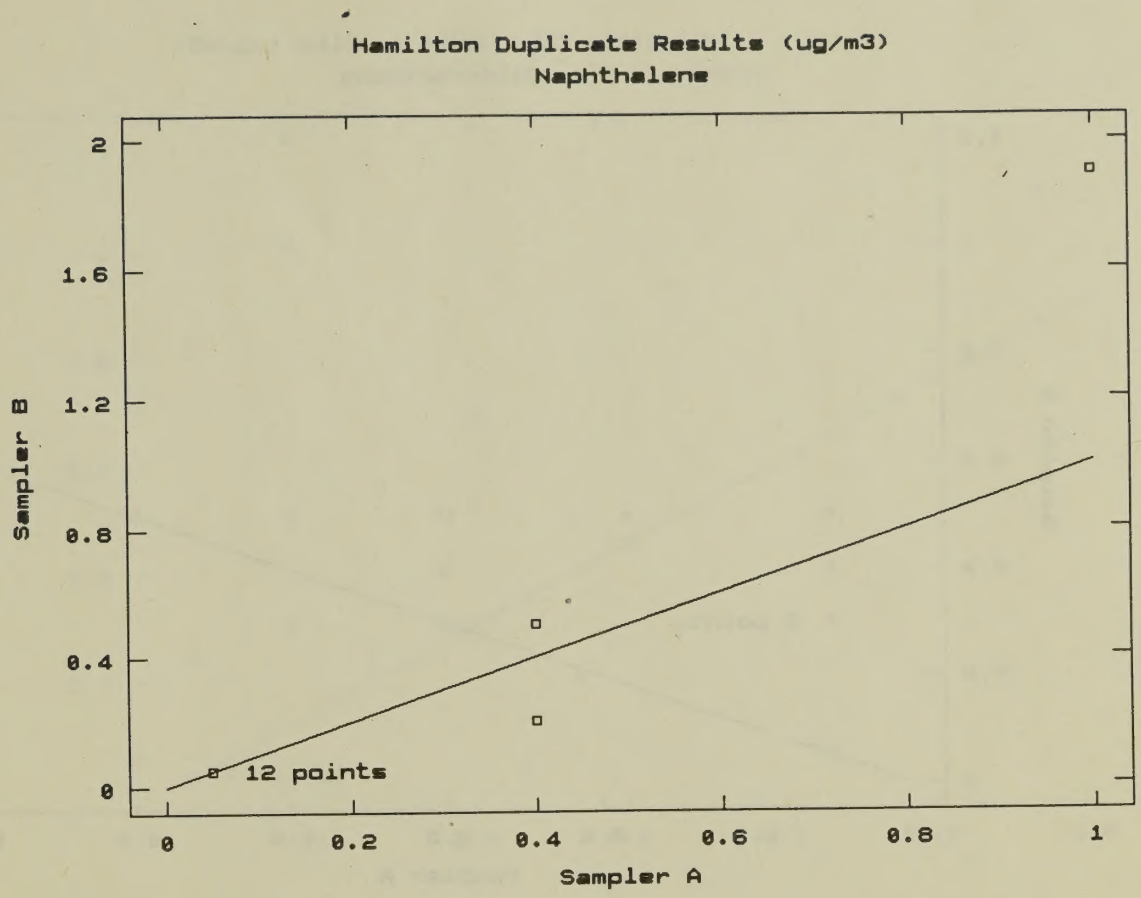

Hamilton Duplicate Results (ug/m3)
Cyclohexane
Sampler B
Sampler A
2 points
2 points
0
0.2
0.4
0.6
0.8
1
1.2

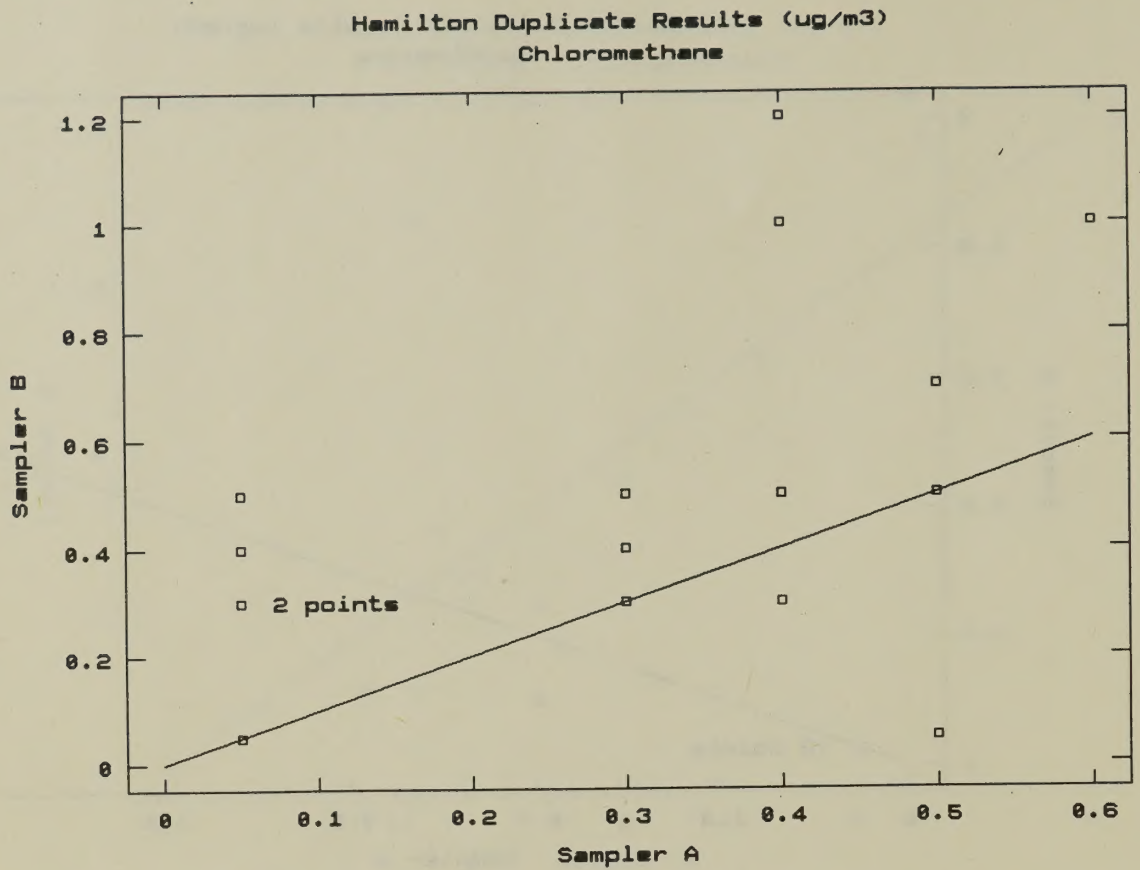

Hamilton Duplicate Results (ug/m3)
Hexane
Sampler B
Sampler A
2 points
0
3
6
9
12
15

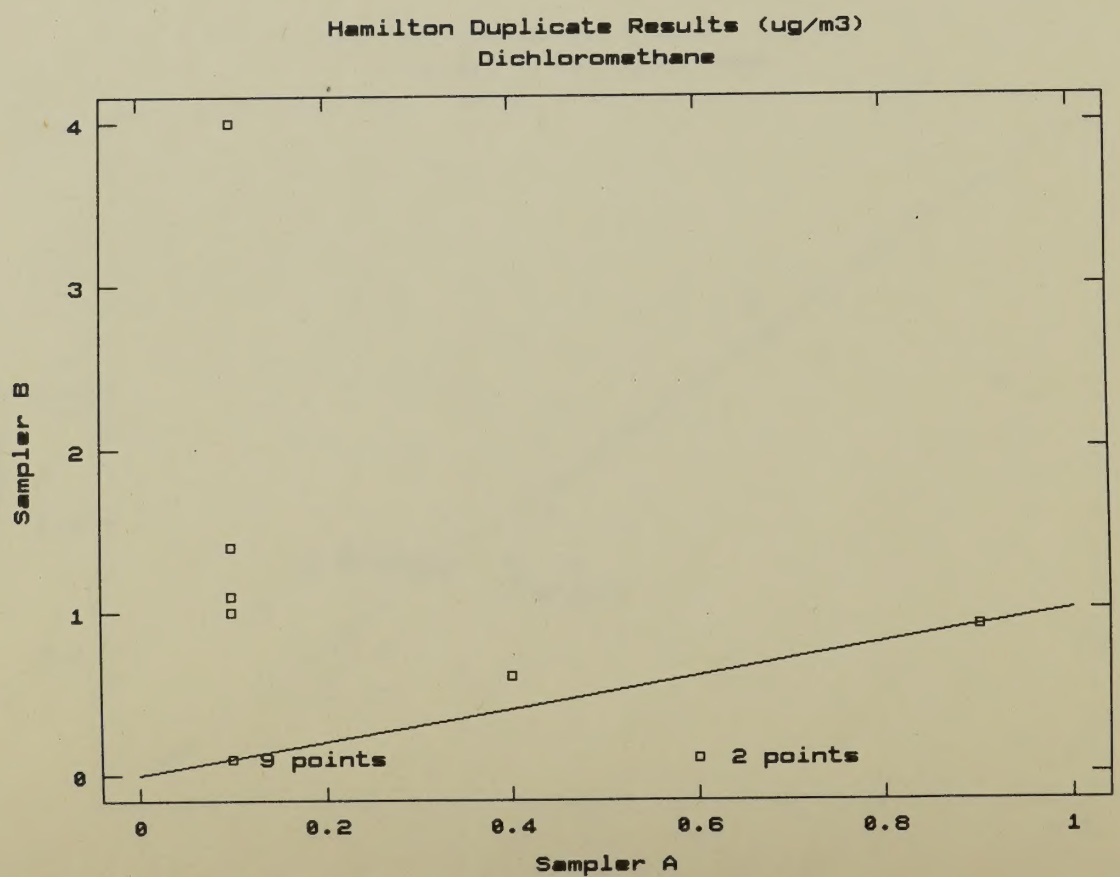

Hamilton Duplicate Results (ug/m3)
Toluene
Sampler B
Sampler A
0
3
6
9
12
15

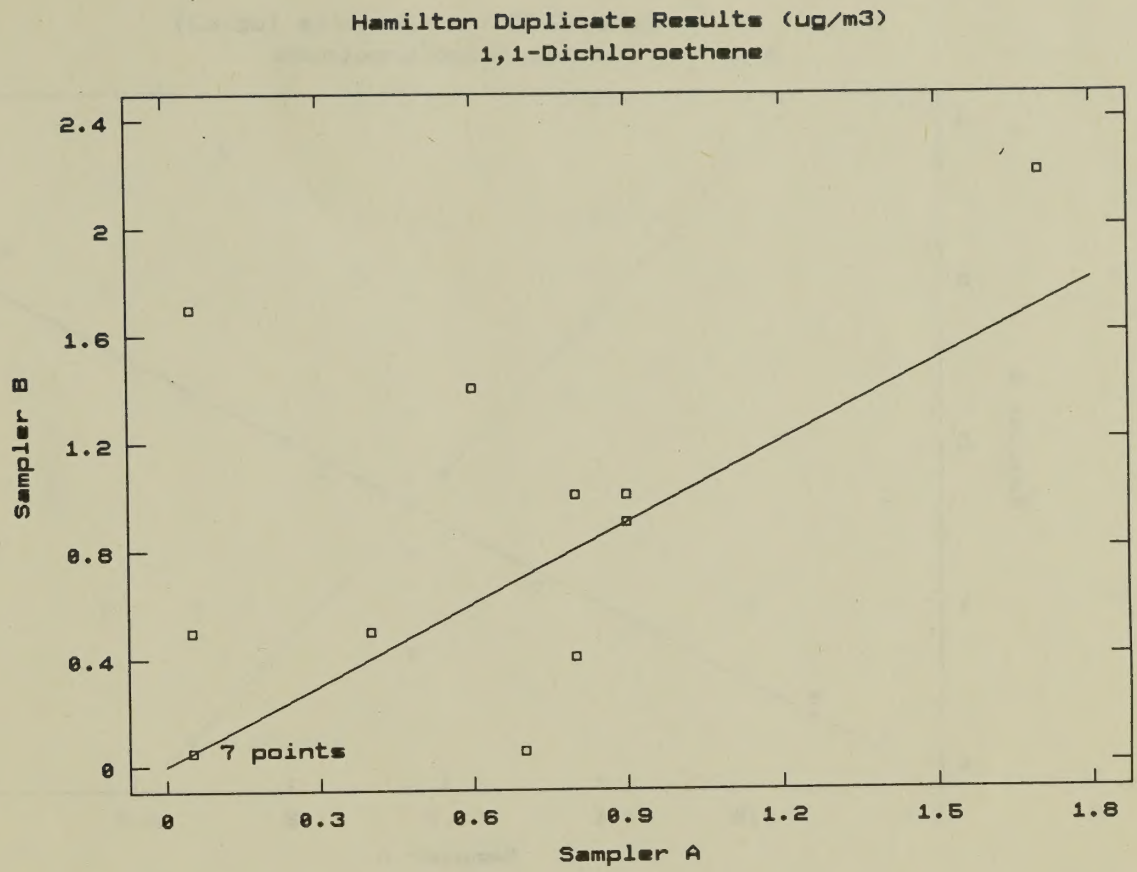

Hamilton Duplicate Results (ug/m3)
1,2,4-Trimethylbenzene
Sampler B
Sampler A
0
1
2
3
4

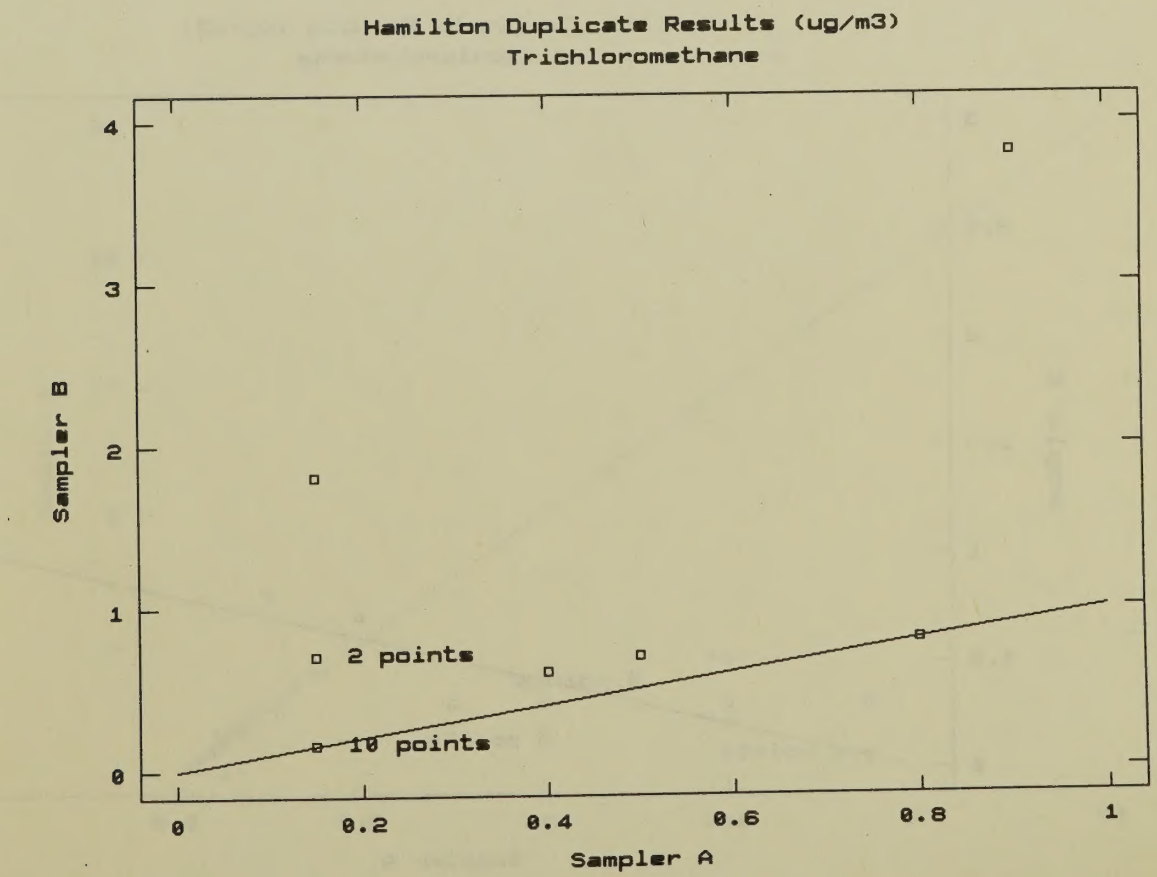

Hamilton Duplicate Results (ug/m3)
1,3,5-Trimethylbenzene
Sampler B
Sampler A
2 points
2 points
0
0.3
0.6
0.9
1.2
1.5

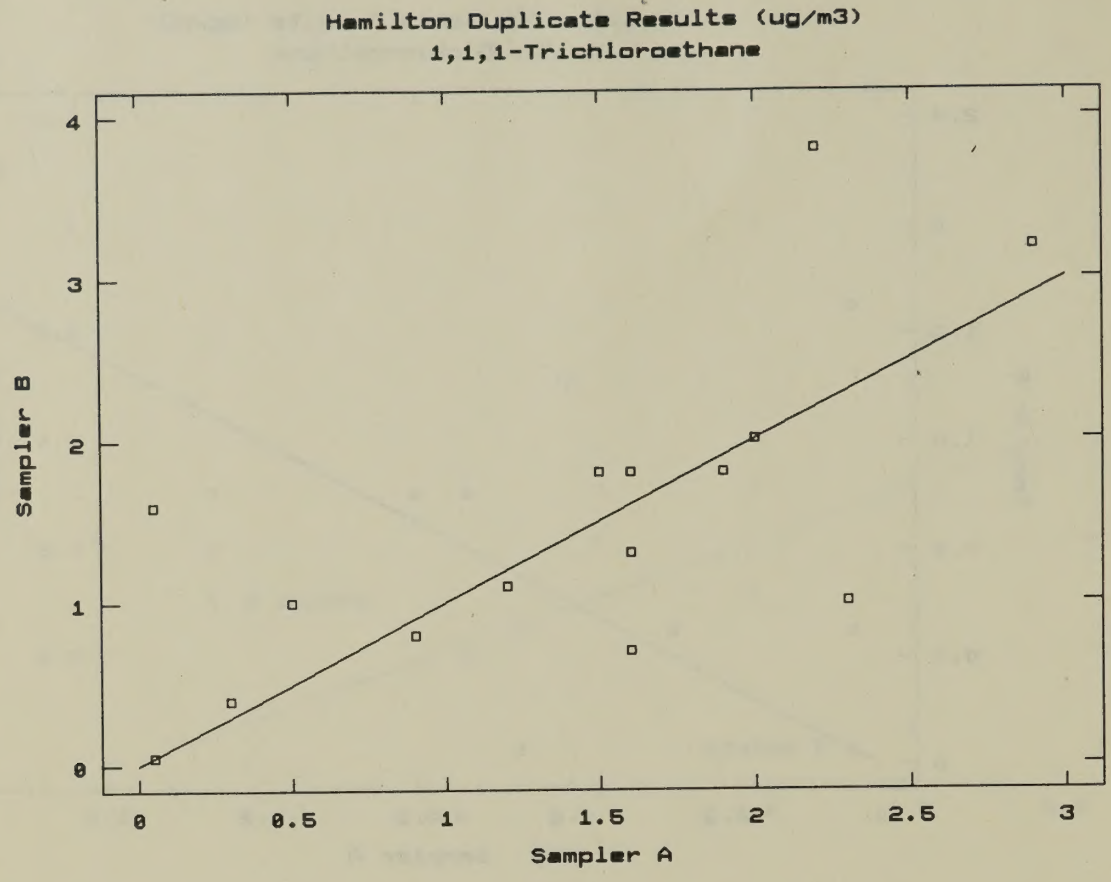

Hamilton Duplicate Results (ug/m3)
Naphthalene
Sampler B
Sampler A
12 points
0
0.4
0.8
1.2
1.6
2
0.2
0.6
1

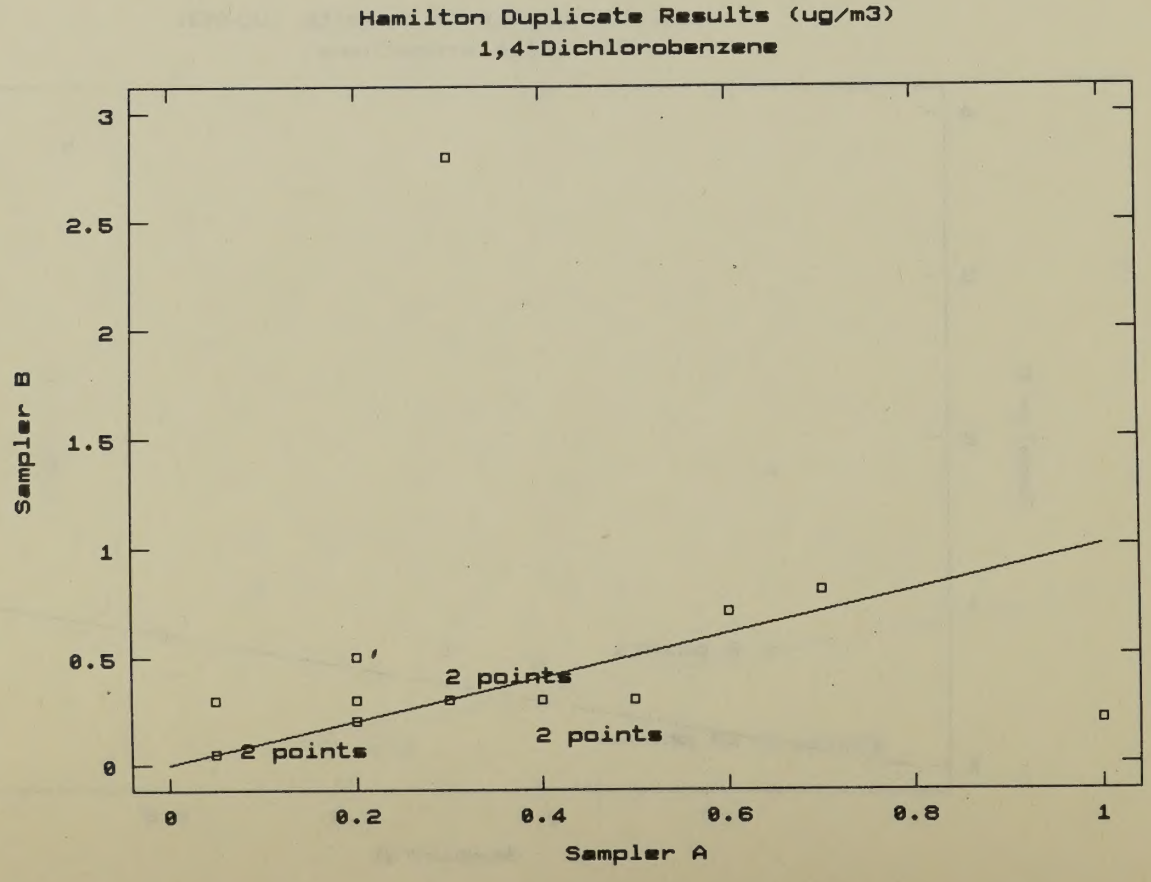

Hamilton Duplicate Results (ug/m3)
Chloromethane
Sampler B
Sampler A
2 points
0
0.2
0.4
0.6
0.8
1
1.2
0.1
0.3
0.5

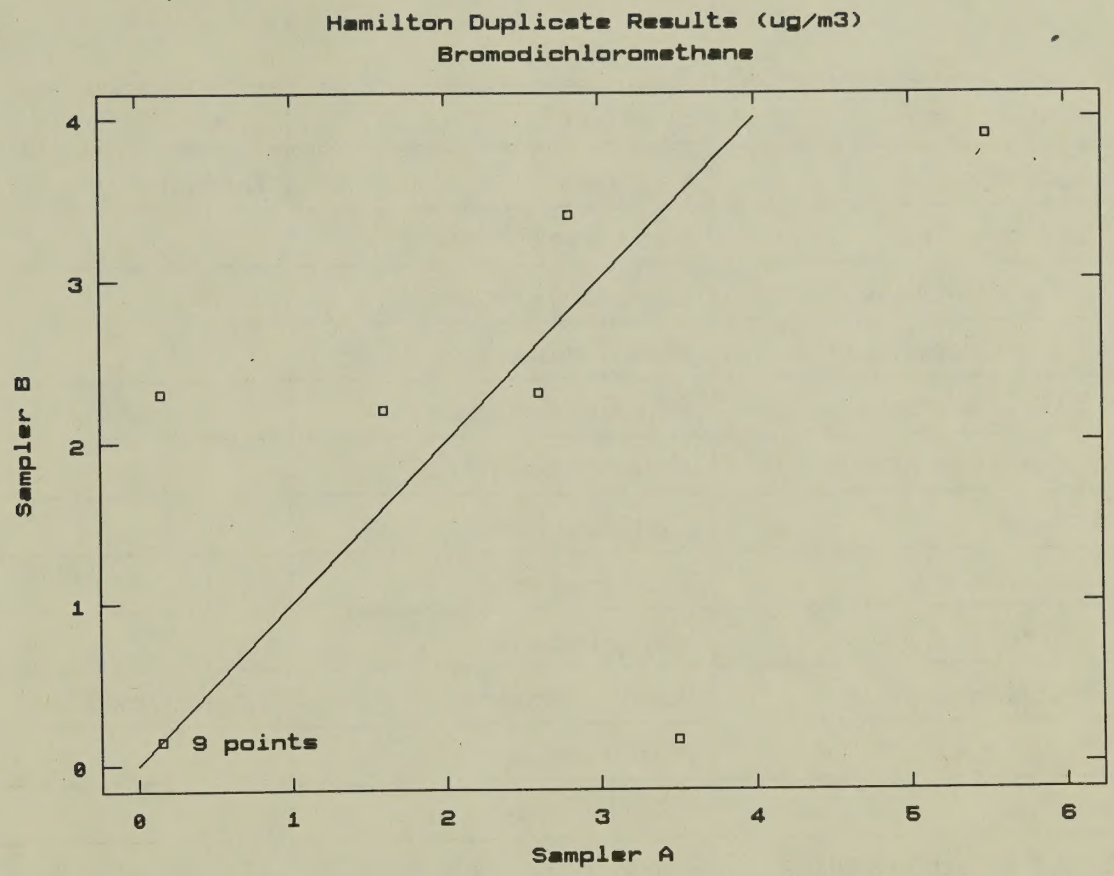

Hamilton Duplicate Results (ug/m3)
Dichloromethane
Sampler B
Sampler A
9 points
2 points
0
1
2
3
4
0.2
0.4
0.6
0.8

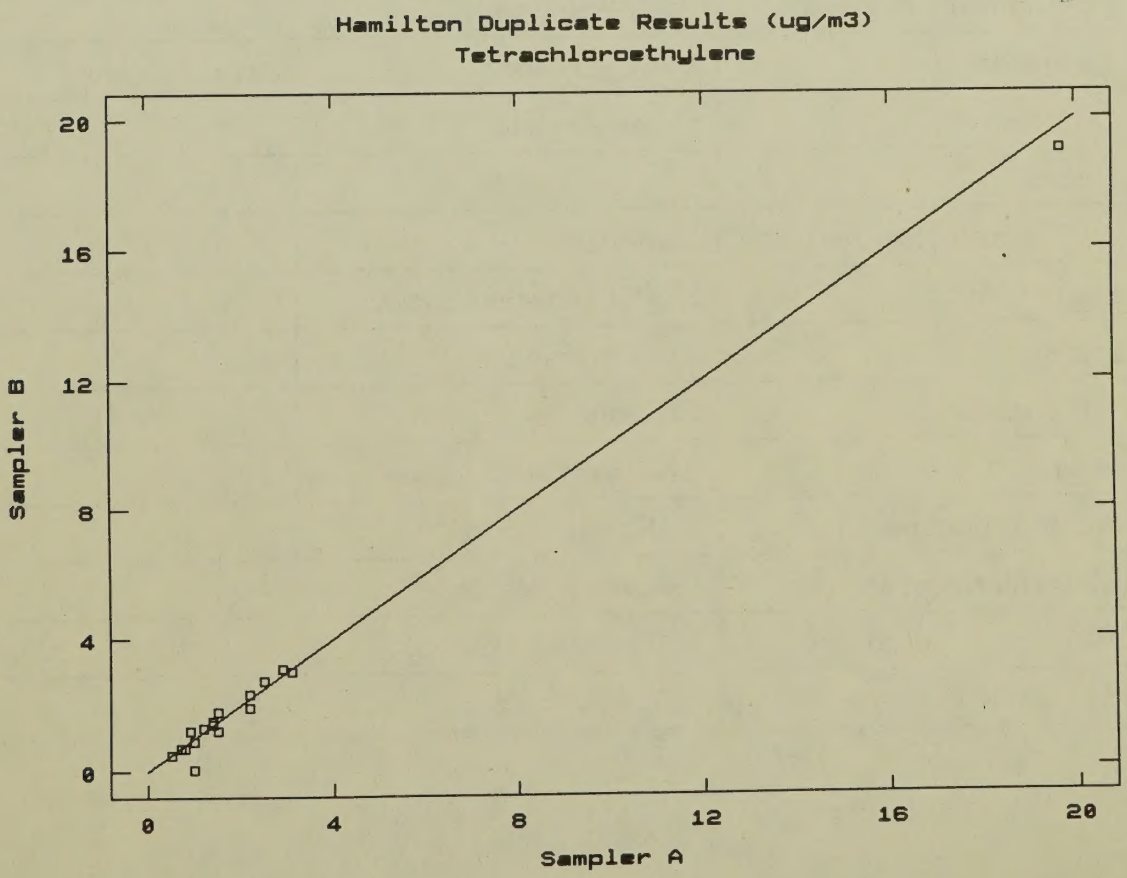

Hamilton Duplicate Results (ug/m3)
1,1-Dichloroethene
Sampler B
Sampler A
2.4
2
1.6
1.2
0.8
0.4
0
0
0.3
0.6
0.9
1.2
1.5
1.8
7 points


Hamilton Duplicate Results (ug/m3)
Trichloromethane
Sampler B
Sampler A
4
3
2
1
0
0
0.2
0.4
0.6
0.8
1
2 points
10 points


Hamilton Duplicate Results (ug/m3)
1,1,1-Trichloroethane
Sampler B
Sampler A
0
1
2
3
4
0
0.5
1
1.5
2
2.5
3


Hamilton Duplicate Results (ug/m3)
1,4-Dichlorobenzene
Sampler B
Sampler A
2 points
2 points
2 points
0
0.5
1
1.5
2
2.5
3
0
0.2
0.4
0.6
0.8
1


Hamilton Duplicate Results (ug/m3)
Bromodichloromethane
Sampler B
Sampler A
9 points
0
1
2
3
4
5
6


Hamilton Duplicate Results (ug/m3)
Tetrachloroethylene
Sampler B
Sampler A
0
4
8
12
16
20

APPENDIX A

| Chemical Name | Synonym | Synonym |
|---|---|---|
| Naphthalene | Naphthene | Tar Camphor |
| Dichloromethane | Methylene chloride | |
| 1,1-Dichloroethane | Ethylidene chloride | |
| 1,1,1-Trichloroethane | Methyl chloroform | |
| 1,2-Dichloroethane | Ethylene dichloride | |
| Carbon Tetrachloride | Tetrachloromethane | |
| Benzene | Cyclohexatriene | |
| Trichloroethylene | Trichloroethene | |
| Toluene | Methylbenzene | |
| Tetrachloroethylene | Perchloroethylene | Tetrachloroethene |
| Ethylbenzene | Phenyl ethane | |
| o-Xylene | 1,2-Dimethylbenzene | |
| 1,1,2,2-Tetrachloroethane | Acetylene tetrachloride | |
| 1,3-Dichlorobenzene | m-Dichlorobenzene | |
| 1,2-Dichlorobenzene | o-Dichlorobenzene | |
| 1,2,4-Trimethylbenzene | Pseudocumene | |
| 1,3-Butadiene | Vinyl ethylene | Bivinyl, Divinyl |
| Cyclohexane | Hexamethylene | |
| Hexane | | |
| 1,3,5-Trimethylbenzene | Mesitylene | |
| m+p-Xylene | 1,3+1,4-Dimethylbenzene | |
| Styrene | Vinyl benzene | |
| Trichloromethane | Chloroform | |
| Isoprene | 3-Methyl-1,3-Butadiene | |
| Bromodichloromethane | Dichlorobromomethane | |
| 1,2-Dichloropropane | Propylene dichloride | |
| cis-1,3-Dichloropropene | 1,3-Dichloropropylene | 1,3-Dichloropropene |
| 1,4-Dichlorobenzene | p-Dichlorobenzene | |

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